

Unifying explanation for carrier relaxation anomaly in gapped systems

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(Dated: February 14, 2012)

We develop a theory to describe energy relaxation of photo-excited carriers in low-temperature ordered states with band gap opening and formulate carrier relaxation time τ near and below transition temperature T_c by quantifying contributions from different carrier-phonon scatterings to the relaxation rate. The theory explains anomalous experimental observations of τ in gapped systems. Transverse acoustic (TA) phonon modes play a crucial role in carrier relaxation; their heat capacity determines τ -divergence near T_c . The theory is validated by fitting τ of fullerene polymers onto a theoretical curve.

PACS numbers: 78.47.-p, 63.20.kk, 71.45.Lr, 74.25.Gz

The nonequilibrium dynamics of photo-excited carriers in solids has attracted considerable research interest in the field of condensed matter physics. These dynamics are governed by multiple scatterings of carriers and energy transfer to the phonon field, both of which are quantified by the carrier relaxation time τ_{exp} and its temperature (T) dependence. Usually anomalous T -dependence of τ_{exp} is observed in many *gapped systems*, for example, phase-ordered systems showing an energy gap opening in the electron band below the transition temperature T_c . It has been found that a wide variety of superconductors [1–12] and density-wave compounds [13–19] show diverging behavior of τ_{exp} near T_c , as confirmed by femtosecond time-resolved optical spectroscopy [1, 4, 5, 7–17, 19]. The divergence of τ_{exp} in these gapped systems is believed to result from recursive energy transfer between electrons and phonons. Photo-excited electrons having high energy emit a number of phonons through relaxation from above to below the energy gap. Conversely, relaxed electrons can be re-excited above the gap by absorbing phonon energy. This phonon emission-reabsorption process becomes efficient near T_c because of the small gap energy, and thus, it suppresses the relaxation of carriers, extending τ_{exp} significantly. This anomalous phonon-mediated relaxation in gapped systems is called the phonon bottleneck effect. This bottleneck enables the reproduction of these experimental observations of τ_{exp} in various gapped systems that exhibit τ_{exp} -divergence at T_c .

There exists, however, a distinct class of gapped systems such as Tl-based superconductors [2, 6] and C_{60} -related materials [3, 18] that, instead of showing τ_{exp} -divergence at T_c , show monotonic increases in τ_{exp} with cooling across T_c . In light of the bottleneck, the monotonic variation in τ_{exp} near T_c appears controversial, leading to the questions of why the τ_{exp} -divergence vanishes in a portion of gapped systems despite well-defined energy gap formation at the Fermi level and whether the bottleneck concept is completely invalid in these gapped systems. Theoretical studies have been unable to satisfactorily answer these two questions over the last decade.

In this Letter, we develop a theory of photo-excited carrier relaxation dynamics with the objective of resolving the abovementioned issues. We postulate that the lack of τ_{exp} -divergence even in gapped systems can be ascribed to the presence of transverse acoustic (TA) phonon modes. Further, we state that an ensemble of TA modes in gapped systems serves as a high-capacity thermal sink, and energy release to the sink from other phonon modes facilitate efficient cooling of carriers, in other words, a significant reduction in τ_{exp} close to T_c . The proposed theory is validated by the quantitative agreement with experimental data of τ_{exp} for peanut-shaped C_{60} polymers, a typical charge density wave (CDW) material that does not show any carrier relaxation anomalies.

First, we briefly review the conventional bottleneck concept for τ_{exp} -divergence. It is based on the assumption that photo-excited carrier relaxation in gapped systems is regulated by the anharmonic slow decay of phonons [1, 20]. By the absorption of a pump laser photon, electrons in the valence band are excited far above the initial states, and they rapidly accumulate in the upper end of the gap through carrier-carrier and carrier-phonon interactions. Then, the carriers emit high-energy phonons (HEPs) whose energies are higher than the gap width 2Δ to relax into the lower end of the gap. The HEPs produced can be reabsorbed to create new carriers above the gap [see Fig. 1(a)] or they can decay in an anharmonic manner into low-energy phonons (LEPs) that no longer excite carriers because their energy is lower than 2Δ [see left-hand side panel in Fig. 1(b)]. If the reabsorption probability per unit time is much larger than the inverse of the anharmonic decay time (τ^{-1}), photo-excited carriers and HEPs settle in nearly steady states that obey the Fermi and Bose distribution functions, respectively, with temperature T' that is higher than the lattice temperature T [1]. Meanwhile, LEPs obey the Bose distribution function with T , because they remain unperturbed after the laser pulse incident. Consequently, the carrier relaxation is dominated by the energy transfer from HEPs to LEPs, that is, $\tau_{\text{exp}} \simeq \tau$, which is described

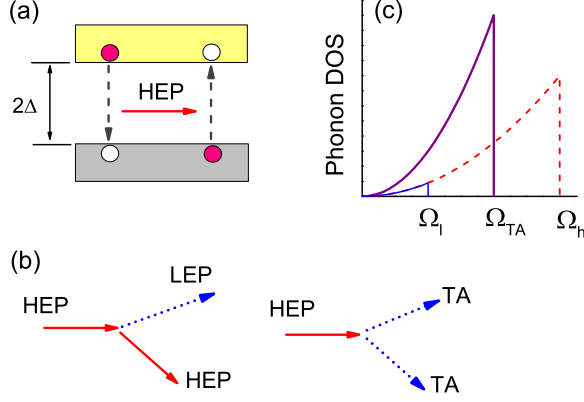


FIG. 1: (Color online) (a) Emission-reabsorption process of HEPs across the energy gap with width 2Δ . (b) Diagram of three-phonon scattering processes through which HEPs dissipate. Only the scatterings that involve TA modes are relevant to the lack of divergence in τ . (c) Phonon density of states of TA modes with cutoff frequency Ω_{TA} , and those of LA modes with Ω_h . The maximum frequency of the LEP is Ω_l (see text for its definition).

by the time evolution of the two temperatures, that is, $T' = T'(t)$ and $T = T(t)$.

It should be emphasized that in the conventional bottleneck concept, only longitudinal acoustic (LA) phonon modes are considered. Here, we point out the unnoticed but important role of TA phonon modes in the HEP's decay [see right-hand side panel in Fig. 1(b)]. Because TA phonon modes generate no density modulation in the lattice, they cannot interact with photo-excited carriers within the deformation potential theory. This fact im-

plies that TA modes serve as a thermal receiver into which HEPs can dissipate, as a result of which the τ -divergence vanishes even at T_c . Below, we prove that this holds true in certain gapped systems.

To formulate the anharmonic decay time τ of HEPs, we consider the time evolution of the phonon distribution function. Following the above discussion, we divide phonon excitations into two groups. One group consists of HEPs ($\Omega_l < \omega_{\mathbf{q},LA} < \Omega_h$) in equilibrium temperature at T' that can participate in the reabsorption process. The other group involves TA modes ($\omega_{\mathbf{q},TA} < \Omega_{TA}$) and LEPs [$\omega_{\mathbf{q},LA} < 2\Delta/\hbar (\equiv \Omega_l)$] in equilibrium at T that do not participate in the reabsorption process. Here, $\omega_{\mathbf{q},TA}$ and $\omega_{\mathbf{q},LA}$ represent the phonon dispersion relations, where \mathbf{q} is the wavevector. Ω_h, Ω_l , and Ω_{TA} are the cutoff frequencies for the HEP, LEP, and TA modes within the Debye approximation, respectively. The distribution functions for the two groups are given by

$$n(\omega_{\mathbf{q},j}) = \left[\exp\left(\frac{\hbar\omega_{\mathbf{q},j}}{k_B x}\right) - 1 \right]^{-1}, \quad (1)$$

with an appropriate variable $x = T$ or T' .

The rate of change in $n(\omega_{\mathbf{q},j})$ due to phonon-phonon collisions is written as [21]

$$\frac{\partial n(\omega_{\mathbf{q},j})}{\partial t} = J_{\text{col}}[n(\omega_{\mathbf{q},j})]. \quad (2)$$

The collision integral $J_{\text{col}}[n(\omega_{\mathbf{q},j})]$ describes three-phonon scattering, and it is defined by

$$J_{\text{col}}[n(\omega_0)] = \frac{2\pi}{\hbar N^2} \sum_{\mathbf{q}_1, \mathbf{q}_2, j_1, j_2} |w_{i \rightarrow f}|^2 \left(\frac{1}{2} S_A + S_B \right), \quad (3)$$

where

$$S_A = \{[n(\omega_0) + 1]n(\omega_1)n(\omega_2) - n(\omega_0)[n(\omega_1) + 1][n(\omega_2) + 1]\} \delta(\hbar\omega_0 - \hbar\omega_1 - \hbar\omega_2), \quad (4)$$

$$S_B = \{[n(\omega_0) + 1][n(\omega_1) + 1]n(\omega_2) - n(\omega_0)n(\omega_1)[n(\omega_2) + 1]\} \delta(\hbar\omega_2 - \hbar\omega_0 - \hbar\omega_1). \quad (5)$$

Here, $\omega_s (s = 0, 1, 2)$ is an abbreviation of $\omega_{\mathbf{q}_s, j_s}$, and $w_{i \rightarrow f}$ is the matrix element between the initial and the final state [22].

Note that J_{col} regulates the time evolution of the total energy through the relationship

$$\frac{\partial}{\partial t}(E_{LA} + E_{TA}) = \sum_{\mathbf{q}(LA)} \hbar\omega_{\mathbf{q},LA} J_{\text{col}} + \sum_{\mathbf{q}(TA)} \hbar\omega_{\mathbf{q},TA} J_{\text{col}}, \quad (6)$$

where the first and second summations on the right-hand side run over \mathbf{q} s satisfying $0 < \omega_{\mathbf{q},LA} < \Omega_l$ and $0 <$

$\omega_{\mathbf{q},TA} < \Omega_{TA}$, respectively. The energy E_j is defined by

$$E_j = \sum_{\mathbf{q}(j)} \hbar\omega_{\mathbf{q},j} n(\omega_{\mathbf{q},j}) = \int_0^y \hbar\omega n(\omega) \rho_j(\omega) d\omega, \quad (7)$$

where $y = \Omega_{TA} (\Omega_l)$ for $j = \text{TA} (\text{LA})$. ρ_j is the density of states defined by

$$\rho_j(\omega) = \alpha_j \omega^2 \theta(z - \omega), \quad \left(\alpha_j = \frac{3\nu_j N}{z^3 \sum_{j'} \nu_{j'}} \right), \quad (8)$$

where $z = \Omega_{TA} (\Omega_h)$ for $j = \text{TA} (\text{LA})$, $\nu_{j'}$ is the number of phonon branches participating in the three-phonon

scattering, N is the number of unit cells, and θ is the Heaviside step function; the total density of states is given by $\rho = \rho_{\text{TA}} + \rho_{\text{LA}}$ [see Fig. 1(c)], satisfying the normalization condition $1 = \int \rho(\omega) d\omega / N$. The Debye approximation we have used in Eq. (8) is valid when $k_B T < \hbar \Omega_{\text{TA}} (< \hbar \Omega_h)$, which holds for many gapped systems below T_c . We simplify $n(\omega)$ in Eq. (7) as $k_B T / \hbar \omega$ [1] to obtain $E_j = C_j T$, where $C_j = k_B \alpha_j y^3 / 3$ (k_B is the Boltzmann constant). In addition, we focus on the fact that each sum in Eq. (6) gives a non-zero value only when one or two HEPs contribute to the three-phonon scattering represented by J_{col} [see Fig. 1(b) as an example]. As a result, Eq. (6) is rewritten as [23]

$$\frac{\partial T(t)}{\partial t} = \frac{1}{\tau} [T' - T(t)], \quad (9)$$

$$\tau = \frac{C_{\text{LA}} + C_{\text{TA}}}{I_{\text{LA}} + I_{\text{TA}}}, \quad (10)$$

using the definitions

$$I_{\text{LA}} = w_1^2 \gamma_0 (V_A T + V_B T'), \quad (11)$$

$$I_{\text{TA}} = w_2^2 \gamma_1 (V_C T + V_D T') + w_2^2 \gamma_2 V_E T, \quad (12)$$

where $\gamma_k = 2\pi k_B^2 \alpha_{\text{LA}}^{3-k} \alpha_{\text{TA}}^k / (\hbar^3 N^2)$. T' is given by

$$k_B T' = -\frac{\Delta}{\ln(\epsilon + e^{-\Delta/k_B T})}, \quad (13)$$

where ϵ is the dimensionless photoexcitation energy [1]. To derive Eqs. (11) and (12), we assumed that the matrix element is momentum independent, that is, $w_{i \rightarrow f} \equiv w_1$ (or w_2) = const. when TA modes are absent from (join in) the three-phonon scattering. V_X ($X = A$ to E) in Eqs. (11) and (12) are functions of $\Omega_l, \Omega_{\text{TA}}$, and Ω_h .

Equation (10) is the main finding of this study, because it clearly shows the contribution of TA phonon modes to carrier relaxation. Figure 2(a) shows the T -dependence of τ that we have formulated in Eq. (10). The parameter p ($\equiv w_2/w_1$) is the coupling strength through which the HEPs decay into TA modes, and it is tuned from 0 to 0.5 in increments of 0.1. With an increase in p , the magnitude of τ decreases over the entire T range. When p is smaller (larger) than ~ 0.3 , τ increases (decreases) as T approaches T_c from below. The most significant phenomenon is the drastic reduction in τ at T_c with increasing p . In fact, τ at T_c is inversely proportional to p^2 , as shown in Fig. 2(b). These results indicate that the lack of τ -divergence at T_c is attributable to efficient phonon-phonon coupling between the HEP and the TA mode characterized by p .

To explain the microscopic mechanism for the lack of divergence, in Fig. 2(c), we show the T -dependence of the magnitude of I_{LA} and I_{TA} given in Eqs. (11) and (12). Here, $I_{\text{LA(TA)}}$ quantifies the efficiency of the HEP's energy dissipation through the anharmonic interaction with LA (TA) phonon modes. In the limit of $T \rightarrow T_c$

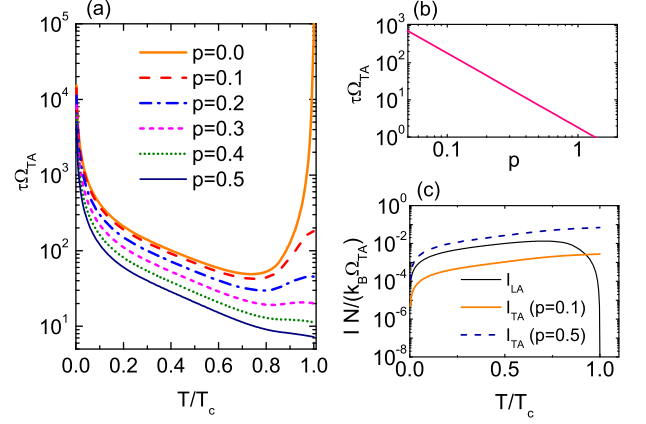


FIG. 2: (Color online) (a) Numerical result of $\tau(T)$ based on Eq. (10). See text for detailed numerical conditions. (b) Inverse square law of τ at $T = T_c$ with respect to p . (c) T -dependence of I_{LA} and I_{TA} defined by Eqs. (11) and (12). Because I_{TA} differs from zero at $T = T_c$, the τ -divergence at T_c is strongly suppressed.

(that is, $\Delta \rightarrow 0$), I_{LA} vanishes (irrespective of p) but I_{TA} converges to a finite value as long as $p \neq 0$. Therefore, we obtain a non-diverging τ at T_c if $p \neq 0$, which readily follows from Eq. (10). When $p = 0$, on the other hand, $I_{\text{TA}} \equiv 0$ for arbitrary T [because $I_{\text{TA}} \propto w_2^2$; see Eq. (12)]. In this case, $I_{\text{LA}} = I_{\text{TA}} = 0$ at T_c so that $\tau \rightarrow \infty$ at T_c . We thus conclude that the anharmonic decay of HEPs to TA modes plays a prominent role in the efficient cooling of HEPs as well as in determining the significance of the τ -divergence at T_c .

Upon reducing the temperature to zero, the energy dissipation of HEPs gradually reduces due to monotonic decreases in I_{LA} and I_{TA} [see Fig. 2(c)]. The decrease in $I_{\text{LA(TA)}}$ is attributed to the reduced phonon population, which results in a monotonic increase in τ at low T , as shown in Fig. 2(a). A similar increase has been found in various gapped systems [2–5, 10–12, 15, 18], and it is attributable to the inefficient cooling of HEPs.

Now, we apply the proposed theory to photo-excited carrier relaxation in quasi one-dimensional C_{60} polymers. It was previously observed in experiments [24] that the C_{60} polymers undergo the CDW transition [25] at $T_c = 60\text{K}$, forming a well-defined energy gap at the Fermi level. This result implied the possibility of τ_{exp} -divergence at 60K; nevertheless, optical pump-probe investigations [18] of the C_{60} polymers revealed a monotonic variation in τ_{exp} near T_c , whose origin has yet to be clarified. This problem is solved by considering that the twisting phonon modes of the C_{60} polymer [26] play the same role as the above-described TA modes. Figure 3 shows the numerical reproduction (indicated by lines) of the experimental data [18] (indicated by circles) of the T -dependent τ_{exp} of the C_{60} polymers. An over-

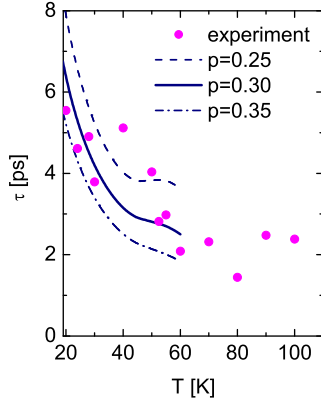


FIG. 3: (Color online) Experimental data of τ_{exp} in the C_{60} polymer (after Ref. [18]) and their numerical reproduction based on Eq. (10). The data for $T \leq T_c = 60\text{K}$ fits the theoretical curve with $p = 0.3$.

all agreement between the theory and the experiments is obtained by assuming $p \sim 0.3$. The other parameters we used are $\Omega_{\text{TA}} = 220\text{cm}^{-1}$, $\Omega_h = 360\text{cm}^{-1}$, and $2\Delta(0) = 360\text{K}$; the first two values were estimated from the phonon model for 1D C_{60} polymers [26], and the last value gives $2\Delta(0)/k_B T_c = 6$ consistent with many CDW compounds [27].

The generality of Eq. (10) is of great importance. It is applicable to τ_{exp} in other gapped systems such as TI-based cuprate superconductors [2, 6] and the solid fullerenes K_3C_{60} and Rb_3C_{60} [3]. Even these materials show a lack of τ_{exp} -divergence; however, no theoretical studies have attempted to clarify their relaxation anomalies. We believe that the proposed theory will serve as a unified framework for nonequilibrium carrier dynamics in gapped systems.

In conclusion, we have developed a theory to describe the energy dissipation from HEPs ($\hbar\omega_{q,\text{LA}} > 2\Delta$) to LEPs ($\hbar\omega_{q,\text{LA}} < 2\Delta$) and TA modes in gapped systems below T_c . This theory enables the evaluation of the T -dependence of τ as a function of the coupling strength $p \equiv w_2/w_1$ between the HEPs and the TA modes, and it explains the crossover between the diverging and the non-diverging behaviors of photo-excited carrier relaxation. The latter behavior can quantitatively account for the anomalous carrier relaxation time in C_{60} polymers, as measured by recent pump-probe laser experiments. The coupling between the HEPs and the TA mode also suggests the variation of τ_{exp} -divergence in typical gapped systems.

We thank K. Yakubo, Y. Asano, J. Onoe, K. Ohno, Y. Noda, and T. Matsuura for the helpful discussions. This study was supported by a Grant-in-Aid for Scientific Research from the MEXT, Japan. HS acknowledges the financial support from the Inamori Foundation and the

Sumitomo Foundation.

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